



Pressure-Enhanced Solid Phase Epitaxy: Implications for Point Defect Mechanisms

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derived from SPER measurements agree well with ESR measurements and suggest that combined ESR and SPER measurements could provide a method for depth profiling the doping efficiencies of impurities in amorphous silicon containing a large density of dangling bonds.

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PRESSURE-ENHANCED SOLID PHASE EPITAXY: IMPLICATIONS FOR POINT DEFECT MECHANISMS

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ABSTRACT

We have measured the effects of hydrostatic pressure on the solid phase epitaxial growth (SPEG) rates of undoped Ge(100) and Si(100) into their respective self-implanted amorphous phases. We found that pressure enhances the growth processes in both Si and Ge, with activation volumes equal to $-3.3 \pm 0.3 \text{ cm}^3/\text{mole}$ for Si and $-6.3 \pm 0.60 \text{ cm}^3/\text{mole}$ for Ge. The results of this and other experiments are inconsistent with all bulk point-defect mechanisms, but are consistent with all interface point-defect mechanisms, proposed to date for thermal SPEG. A kinetic analysis of the Spaepen-Turnbull dangling bond mechanism shows it to be a highly plausible model for the growth process.

INTRODUCTION

Studies of post-annealing processes in implantation-amorphized silicon and germanium [1-6] have established a similar growth process, termed solid phase epitaxial growth (SPEG), for the crystallization of both amorphous phases. SPEG occurs by motion of a planar crystal/amorphous interface. The growth rates are well described by an Arrhenius dependence on temperature, with activation energies of ~ 2.70 and $\sim 2.0 \text{ eV}$ for Si and Ge, respectively. In addition, the effects of dopants [3] and ion irradiation reported in recent ion-beam studies [7-11] on the growth process in Si have been well established. Many experimental findings have been discussed in a recent review article by Olson and Roth [3]. Despite all of the experiments, there is no agreement on the mechanism of the growth process. There have been many atomistic models [2,6,12-16] proposed to explain the process. These models invoke different types of defects whose creation or transport at or to the c/a interface might be the rate-limiting step of the growth process. In Table I we list some models that have been proposed to explain SPEG in Si.

The pressure dependence of a kinetic process bears directly on the atomistic mechanisms. Temperature-dependence experiments performed at ambient pressure reveal the activation energy, $\Delta E^* = -k_B(\ln v)/T$, while isothermal pressure-dependence experiments reveal the activation volume, $\Delta V^* = -k_B T(\ln v)/\Delta P$. Here v is the kinetic rate constant for any process (the interface velocity in the case of SPEG); k_B is Boltzmann's constant; P and T are pressure and temperature. In this paper, we will review our experimental results on the pressure-enhanced SPEG process in undoped Si and Ge. Detailed descriptions of the experiment and observations have been reported elsewhere [17-19]. We will then examine various proposed models in light of our pressure measurements, results of other experimental work, and some kinetic arguments. We are led to strong conclusions regarding the tenability of the various models of thermal SPEG.

EXPERIMENT AND RESULTS

Single crystal (100)-oriented undoped Si and Ge wafers were polished on both sides to a thickness of $25 \pm 40 \mu\text{m}$. Self-implantation produced uniform amorphous layers $\sim 300 \text{ nm}$ thick in Si and 800 nm thick in Ge. Wafers were diced or cleaved into many microscopic pieces (about $250 \mu\text{m} \times 250 \mu\text{m}$) to fit into the diamond anvil cell.

Crystal growth occurred in a high-temperature and high-pressure diamond anvil cell (DAC) [20]. Fluid argon, loaded cryogenically, is used as the pressure transmission medium. The ruby fluorescence technique [21], which measures the pressure-induced wavelength shifts of the ruby fluorescence lines excited by a He-Cr laser (441 nm), was used to measure the pressure on the sample. The cell was heated by a flexible resistive heating wire wrapped around the pressure chamber. A chromel-alumel thermocouple, placed next to the diamond and in contact with the metal gasket, was used to monitor the temperature.

Table 1. Defects Proposed for Solid Phase Epitaxial Growth and Conclusions Drawn from this Study.

Mechanism	Conclusions for Si	Conclusions for Ge
Dangling Bonds at c/a interface [12]	Highly Plausible	Highly Plausible
Kink Sites at c/a Interface [13]	Possible	Possible
Vacancies in Crystal [6]	Highly Implausible	Impossible
Interstitials in Crystal	Highly Implausible	Highly Implausible
Vacancies in Amorphous Phase [14]	Impossible	Impossible
Interstitials in Amorphous Phase	Impossible	Impossible
Dangling Bonds in Amorphous Phase [15]	Impossible	Impossible
Floating Bonds in Amorphous Phase [16]	Impossible	Impossible

The *in situ* optical interferometry, or time-resolved reflectivity (TRR), technique developed by Olson *et al.* [22] was used to monitor the moving c/a interface. For silicon, a single line He-Ne laser (5 mW, wavelength $\lambda = 692.8$ nm) was used. For Ge, we used a two-line He-Ne laser source (red: 2 mW, $\lambda = 692.8$ nm, and infrared (IR): 0.5 mW, $\lambda = 1162$ nm). The visible red line enabled us to locate and focus the laser onto the microscopic sample in the cell. The IR line was used for interferometry.

Figures 1 (a) and (b) are isothermal plots of v to determine the activation volumes (ΔV^*) of SPEEG in Si and Ge, respectively. In Si we find $\Delta V^* = -3.3 \pm 0.3 \text{ cm}^3/\text{mole}$, which is -28% of Ω_{Si} , the atomic volume of crystalline Si (c-Si). In Ge we find $\Delta V^* = -6.3 \pm 0.6 \text{ cm}^3/\text{mole}$, which is about -46% of Ω_{Ge} , the atomic volume of crystalline Ge (c-Ge). The negative sign of the activation volumes signifies that the growth rate is enhanced with the application of pressure, as seen clearly from the figures.

DISCUSSION

Implications for bulk point defect mechanisms

For any bulk point defect mechanism of thermal SPEEG in which the process of defect impingement on the interface acts in series with the process of atomic reaction at the interface, the growth rate can be expressed as

$$v \propto \frac{k_d k_i}{k_d + k_i} \quad (1)$$

where k_d is the rate of bulk generation and transport of defects to the interface and k_i is the interface reaction rate. In general, both k_d and k_i are expected to have Arrhenius form. Their product will have Arrhenius form if one of these rate constants is negligibly small with respect to the other (the unlikely alternative is that they have identical activation energies - and volumes). That Si SPEEG has a single activation energy over 10 decades in velocity [3] is strong evidence for only one of these processes being significantly rate-limiting. If the rate-limiting step is the interface reaction rate, then we don't really have a bulk defect mechanism. That is, concern over how defects get to the interface seems as superfluous as concern over how thermal energy gets to the atoms doing the reacting. If, on the other hand, the rate-limiting step is bulk generation and transport to the

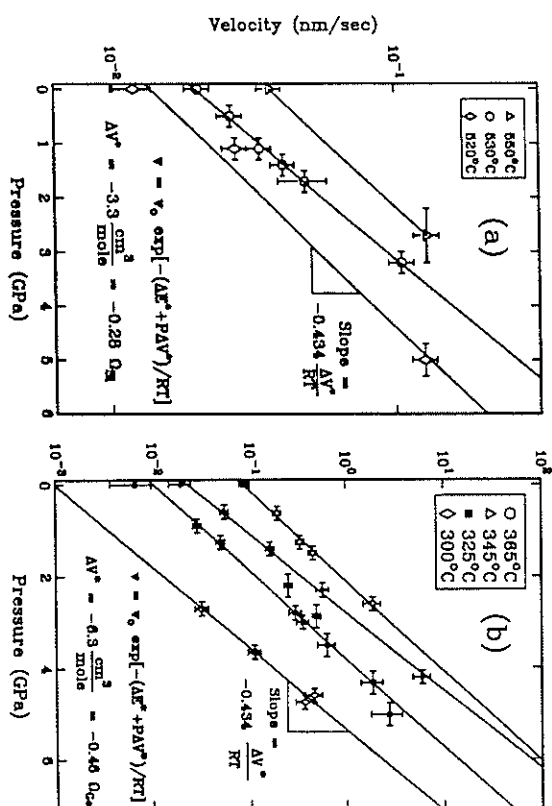


Figure 1. Growth rate vs. pressure in (a) Si; (b) Ge

interface, then we can make direct comparisons of the SPEEG rate with the bulk diffusivity. For both processes, the rate would be given by a product of the concentration of point defects, their mobility, and a geometrical factor. Hence

$$\frac{v}{D_{\text{bulk}}} = \text{constant} \quad (2)$$

Implications for vacancies in Ge. Suni *et al.* [6] adopted the suggestion of Csapregi *et al.* [2] and proposed that the rate limiting step for SPEEG process is the formation and migration of lattice vacancies to the crystal/amorphous interface. Recently Werner *et al.* [23] produced direct evidence for the vacancy mechanism of diffusion by finding a positive activation volume in their high pressure study of germanium self-diffusion. They deduced +0.56 Ω_{Ge} for the activation volume of diffusion via the neutral vacancy. Comparing with the negative activation volume of -0.46 Ω_{Ge} obtained in this study of germanium SPEEG, it is clear that eq. (2) is violated and hence the defects responsible for limiting the self-diffusion rate in the crystal are not the same as those limiting the SPEEG rate.

Implications for vacancies in Si. If SPEEG in Si were controlled by the diffusion of vacancies in the crystal, the observed pressure-enhanced SPEEG would have to be due to pressure reducing the barrier to vacancy motion enough to overwhelm the pressure-reduced vacancy concentration. We can then put an upper limit on the formation volume of the vacancy by realizing that once the barrier to motion cannot be reduced past zero, whereupon something dramatic should happen, e.g., the slope of the SPEEG rate vs pressure isotherm might change sign. The barrier for vacancy migration ΔE_m^* according to Watkins [24], is 0.45 eV for neutral vacancies.

No breaks are observed up to the highest pressure annealing point, $P_{\text{max}} = 50$ kbar at 520°C, in Fig. 1(a). At this point, by requiring $\Delta E_m^* + P_{\text{max}} \Delta V_m^* \geq 0$, we obtain a lower limit for the migration volume of a vacancy: $\Delta V_m^* \geq -0.72 \Omega_{\text{Si}}$. The difference between the measured ΔV^* for SPEEG and ΔV_m^* is then an upper limit on the formation volume:

$$\Delta V_f^0 \leq +0.44 \Omega \text{Si} \quad (3)$$

This value is much smaller than that (0.75 Ω Si) found in a recent total energy calculation [26]. Therefore, in silicon, the formation and transport of crystalline vacancies to the c/a interface is highly implausible to be the rate-limiting step for the SPEEG process.

Implications for Minority Diffusers. There are further considerations for any mechanism involving point defects from the bulk of either phase, for which the defects contribute even a minor amount to self diffusion. If each such defect converts N_f atoms from the amorphous to the crystalline phase upon its arrival at the interface, v of (100)-oriented Si or Ge can be written:

$$v = \left(\frac{1}{2} \Gamma \cdot \frac{C_{\text{c/a}}^D \cdot N_f}{C_0} \right) \cdot \left(\frac{a}{d} \right) \quad (4)$$

where Γ is the jump frequency of the defect; $C_{\text{c/a}}^D$ is the defect concentration at the c/a interface; C_0 is the atomic concentration (1/ Ω); and a is the crystal lattice parameter. The factor 1/2 comes from the fact that only half of the jumps move a defect toward the interface.

For random-walking defects, their diffusivity is $D = \Gamma d^2/6$, where d is a jump distance which depends on the type of defect. d is related to the nearest neighbor distance λ by $d = f\lambda$, where $\lambda = \sqrt{3}a/4$ and a is the cubic lattice parameter. v can then be re-written in terms of D :

$$v = \frac{\sqrt{3}}{2} \cdot \left(\frac{D}{\lambda} \right) \cdot (C_{\text{c/a}}^D \cdot N_f \cdot \Omega) \quad (5)$$

where f is unity for vacancy, interstitial, vacancy-like, and interstitial-like defects, and about 1/4 for dangling and floating bonds [19].

That defect diffusion contributes to self diffusion allows the placement of an upper limit on the product of the equilibrium defect concentration far away from the interface and their diffusivity (D^0) as given by $D^0 \cdot C_{\text{bulk}}^D \leq D^{\text{self}}$. C_0 , where D^{self} is the measured bulk self-diffusion coefficient. Since the interface acts like a sink for the defects, $C_{\text{c/a}}^D \leq C_{\text{bulk}}^D$. Combining these inequalities with equation (5) yields a lower limit for N_f , the number of rearrangements from each captured defect at the interface, given by

$$N_f \geq \frac{f\Omega}{3} \cdot \frac{D^0}{D^{\text{self}}} \quad (6)$$

We use the available self-diffusion data in c-Si [26] and c-Ge [23] to place lower limits on N_f for mechanisms involving crystal vacancies or interstitials. They are $N_f \geq 3 \times 10^8$ for Si at 803 K, and $N_f \geq 1 \times 10^8$ for Ge at 600 K. This result is based only on two assumptions: that bulk diffusion of the defect controls the SPEEG process, and that defect diffusion also contributes to bulk self-diffusion. Values of N_f much above 10^8 seem highly implausible [27]. So we conclude that mechanisms of thermal SPEEG based on crystal vacancies and self-interstitials are highly implausible. This follows simply because the self-diffusivities in c-Si and c-Ge are way too low to account for the observed growth rates.

Implications of the nonhydrostatic stress effect. Recently, Aziz *et al.* [28] discovered that the SPEEG rate in Si is enhanced by uniaxial tension and reduced by uniaxial compression, in contrast to the enhancement by hydrostatic pressure. Combining the results of these two experiments, the entire activation strain tensor for Si SPEEG was determined. The transition state is "short and fat": the system undergoes a contraction in the direction normal to the interface and an in-plane expansion. The tetragonal symmetry of the transition state is *inconsistent with the formation or motion of any point defect in the bulk of the amorphous phase* so long as the stress is fully relaxed, as measurements indicate [29]. Both the formation and motion of any bulk point defect in a fully-relaxed amorphous phase must be isotropic rather than tetragonal.

Kinetic analysis of dangling bond mechanism

The results indicate that the Spaepen-Turnbull mechanism [12], in which dangling bonds are generated at the interface and migrate along the interface reconstructing the random network into the crystalline network, is one of the two proposed mechanisms that remains tenable. The model also seems highly plausible in light of its predicted negative activation volume: the mobility of dangling bonds is enhanced by pressure through a transition state, in which the dangling bond reaches across a ring to attack a fully-coordinated Si, with a lower local volume [30]. A kinetic

analysis of the model was undertaken [31] to further check its plausibility. In this analysis, v is given by a product of three factors: the fraction of bonds at the interface that reside at a ledge, the probability that such a bond is dangling, and the average velocity of migration of a dangling bond. A single bond breaks to form a pair of dangling bonds, each of which migrates independently, moving a net distance of N_f migration steps and converting N_f atoms from the amorphous to the crystal phase, before becoming annihilated or stuck at one of a fixed number of "traps". The nature of the "traps" is at present uncertain, but unimolecular annihilation kinetics at the "traps" are essential to the success of the model. The result is:

$$v = 2 \sin(\theta) \cdot v_N \cdot \exp\left(\frac{\Delta S_f + \Delta S_m}{R}\right) \cdot \exp\left(-\frac{\Delta H_f + \Delta H_m}{RT}\right), \quad (7)$$

where v_N is the speed of sound, θ is the misorientation from [111], and ΔS_f , ΔS_m , ΔH_f , and ΔH_m are entropies and enthalpies of formation and of motion of dangling bonds at the interface. The predictions of the model are as follows:

Prefactor: to match the measured prefactor for growth, $N_f \cdot \exp\left(\frac{\Delta S_f + \Delta S_m}{R}\right)$ must be approximately 200 for Si and 1200 for Ge. This corresponds to several hundred rearrangements per activation, which is certainly more plausible than 10^8 .

Activation energy: Within the context of the model, the difference between the measured activation energy for SPEEG and the bond energy [32] is the migration energy. This would be 0.36 eV for Si and 0.3 eV for Ge. The former compares well with apparent activation energies of 0.2–0.33 eV for ion-beam-enhanced SPEEG in Si [7,8,11].

Orientation dependence: The model predicts a proportionality between v and $\sin(\theta)$, in agreement with the well-known results of Csepregi *et al.* [11].

Doping dependence: The population statistics of charged dangling bonds at the interface could respond to the doping level through a variety of schemes that have been discussed in the literature. The details are still a matter of debate [6, 13, 15] and are the subject of several papers in this volume [33].

Activation volume: According to the model, the volume of motion is large and negative. Estimates of the formation volume and measurements of the activation volume allow us to place approximate limits on the volume of motion, which should be between -0.3 and -0.5Ω in Si and between -0.5 and -0.7Ω in Ge. Since pressure reduces the barrier to motion, at high enough pressures the barrier will vanish and something wildly nonlinear and presently unpredictable might be observed. The predicted critical pressure is 70–120 kbar in Si and 30–60 kbar in Ge. In fact, Shimomura *et al.* [34] have observed room-temperature metallization of a Si at 100 kbar and of a-Ge at 60 kbar. This may be a coincidence, or it may be a manifestation of athermal motion of dangling bonds at the critical pressure.

CONCLUSIONS

We summarize our conclusions in Table 1. Bulk crystal point defect mechanisms are untenable because of the magnitude and sign of the activation volume for SPEEG and because of the low bulk crystal diffusivity. Bulk amorphous point defect mechanisms are untenable because uniaxial compression reduces v whereas hydrostatic pressure enhances v . Our results are consistent with any mechanism involving defect formation or motion at the interface. A kinetic analysis of the Spaepen-Turnbull dangling bond mechanism shows it to be a highly plausible model for the growth process. We cannot perform a similar kinetic analysis of the Williams-Elliott kink model.

Our conclusions are valid only for thermal SPEEG. Ion beam-enhanced SPEEG may involve, for example, bulk point defects impinging on the interface and converting to dangling bonds. But when the ion beam is turned off, the rate of interface motion is not limited by arrival of these, suddenly-less-numerous defects. Bulk point defect conversion to dangling bonds at the interface, operating in parallel with thermal generation of dangling bonds at the interface, is plausible. In the future, bulk point-defect models of beam-enhanced SPEEG must address the transition to an interface point-defect mechanism as the ion beam is reduced. A more thorough report, including other experimental results and a discussion of other restrictions on bulk point defect mechanisms, will be published soon [35].

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SPECIFIC HEAT AND MELTING TEMPERATURE OF RELAXED AND UNRELAXED SI AMORPHOUS STATES

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ABSTRACT

Direct, picosecond laser measurements of the critical fluence for melting have been performed for the first time, giving unambiguously consistent differences in the energy required for surface melting of relaxed and unrelaxed amorphous silicon. The different optical coupling cannot account for this variation which can only be explained in terms of different melting temperatures. Heating of unrelaxed amorphous silicon samples at temperatures close to the melting point may result in relaxation of the material even when the treatment occurs in the nanosecond time scale. However nanosecond UV irradiation of relaxed and unrelaxed amorphous silicon samples have provided information on the specific heat of the two amorphous states. The melting temperature of unrelaxed amorphous silicon has been derived independently via both picosecond data and via free energy calculations.

INTRODUCTION

In a recent paper [1] we have undertaken a series of precision melting threshold measurements during UV pulsed laser irradiation of relaxed and unrelaxed amorphous silicon (a-Si). The melting threshold of relaxed a-Si resulted 16% higher than that of the unrelaxed one, being this difference the result of a change of both melting temperature and thermal parameters of a-Si upon relaxation. Using particular samples and modelling the heating process with temperature independent thermal parameters, we found out that the variation of the quantity $\sqrt{k c_p}$ (being k the thermal conductivity and c_p the specific heat of a-Si) on going from the unrelaxed to the relaxed state can account for a 12% shift of the melting threshold, whilst the remaining 4% is to be attributed to a different melting temperature. Therefore, if we assume 1470 K as the melting temperature of the relaxed a-Si [2], we estimate, from our data, a decrease of 46 ± 12 K for the melting temperature of unrelaxed a-Si.

In ref.3 we have estimated the thermal diffusion coefficient $D = \frac{k}{\rho c_p}$ (being ρ the mass density of a-Si) to be equal in relaxed and unrelaxed a-Si within a factor of 1.5, i.e. within our experimental accuracy. The difference between the thermal diffusion coefficient of relaxed and unrelaxed a-Si has been recently resolved by more refined measurements [4] which have provided the following values $D^{rel} = (2.53 \pm 0.02) \cdot 10^{-3} \text{ cm}^2/\text{s}$ and $D^{unrel} = (1.78 \pm 0.02) \cdot 10^{-3} \text{ cm}^2/\text{s}$ (the superscript rel and unrel refer to relaxed and unrelaxed a-Si respectively). This information along with the measured $\sqrt{k c_p}$ variation upon relaxation provided the ratio between the specific heat of unrelaxed and relaxed a-Si $\frac{c_p^{unrel}}{c_p^{rel}} = 1.070 \pm 0.015$. The latter estimate allowed us to recalculate the free energy diagram of relaxed and unrelaxed a-Si using the heat of relaxation and crystallization measured by Donovan [2].

In fig.1 the free energy curves of the amorphous states relative to crystal sil-